

## Effect of RF Negative Bias on the Structure and Performance of Diamond-like Carbon Films in ECR plasma

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**Keywords:** Diamond-like carbon films, ECR, RF negative bias, structure and performance.

**Abstract.** Diamond-like carbon films (DLC) were deposited on single crystalline silicon surface under different RF negative bias in microwave electron cyclotron resonance (ECR) plasma source. The chemical structure and morphology were characterized by Fourier transformation infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The friction coefficient of films was measured to examine the film property later. The results show that the smooth and compact deposited films were typical hydrogenated diamond-like carbon with  $-CH_n$  stretching vibration in  $2800-3000\text{cm}^{-1}$ . It is noticed that with the increase of RF bias on the substrate the peak intensity for C-H stretching vibration in spectrum between  $2800\text{cm}^{-1}\sim 3000\text{cm}^{-1}$  increased at the beginning and then decreased, which caused the friction coefficient of the film being smaller and then larger in reverse. In 50W RF biased power one can obtain the maximum  $-CH_n$  peak intensity and the minimum friction coefficient.

### Introduction

Diamond-like carbon (DLC) is a metastable form of amorphous carbon containing a significant fraction of  $sp^3$  bonds [1], and was intense research and development over the last 25 years, because of their excellent properties like high hardness, good wear resistance, very low friction coefficient, high infrared penetrability, good chemical inertness, and high thermal and low electrical conductivity [2, 3]. With these good properties, DLC films have been widely used as wear and corrosion protection coatings of magnetic storage media, IR optics and some special plastic materials to prevent the passing of oxygen and water vapor. Meanwhile more potential applications of DLC film are being developed, such as its use in biological environments [4, 5].

DLC films can be prepared by various techniques, such as ion beam deposition, magnetron sputtering, pulsed laser deposition, radio frequency chemical vapor deposition, and microwave-enhanced plasma chemical vapor deposition. Among these processes, due to the different plasma source, deposition methods and process etc., the structure and properties of the DLC films would show the obvious diversities, thereinto plasma density and plasma power have the maximal effect on the structure and properties of the films in PECVD process [6~8]. In this study, a microwave electron cyclotron resonance (MW-ECR) apparatus was employed to prepare the DLC films. The ECR has several distinct advantages over the conventional plasma techniques, like large area uniformity, high degree of ionization and high ions densities and so on. In addition with RF negative substrate bias the positive ion flux reaching the substrate can be controlled, a dual power sources-plasma enhanced chemical vapor deposition have formed [9]. Therefore the effect of the different RF negative bias on the structure and performance of DLC films was investigated in this paper.

## Experimental Details

The schematic diagram of the experimental equipment is illustrated in Fig. 1. The ECR discharge chamber of diameter in 100mm is located at the top of the deposition chamber. And the deposition chamber is 40 cm in diameter and 55 cm in height. The coils for magnetic field generation are water-cooled. Microwave through waveguide tubes is introduced into the discharge chamber. The temperature on the heated substrate holder is diagnosed through a Pt- Rh thermocouple. And the RF negative bias source is applied to the holder for propose of controllable ion flux and energy.

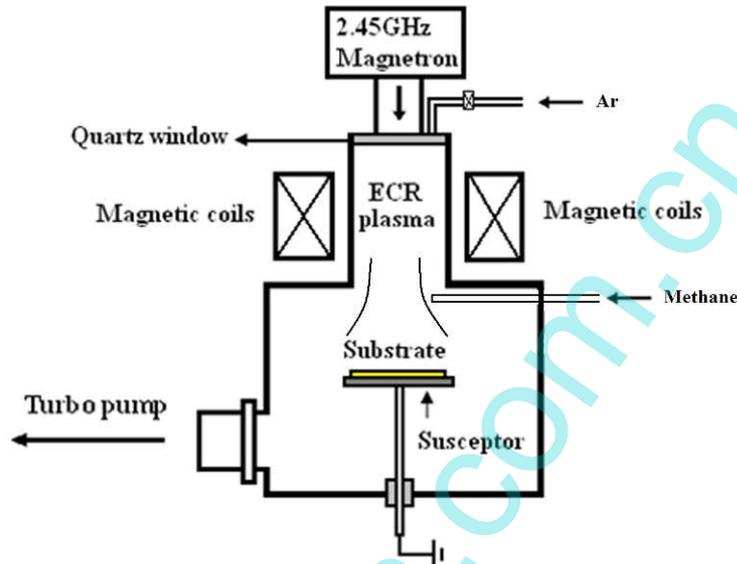


Fig.1. Schematic view of the Microwave-ECR system

Polished silicon (100) wafers were used as substrates. Before the deposition processing, the silicon wafers were ultrasonically cleaned in an acetone, then rinsed in an ethanol, and loaded on holder at last. The base pressure of  $5.0 \times 10^{-4}$  Pa in the chamber is obtained using a turbo molecular pump system. Prior to the DLC film deposition, the surface of the substrate was bombarded by Ar plasma for 15 min under the condition of the ECR power of 600W to remove surface contaminants and oxides. Subsequently the chamber was evacuated to  $5.0 \times 10^{-4}$  Pa again. After Ar was inlet to the discharge chamber and generated plasma, methane was introduced into the deposition chamber to grow the DLC films. The processing conditions are listed in Table 1.

Table 1. Preparation conditions of the DLC films in RF biased ECR plasma.

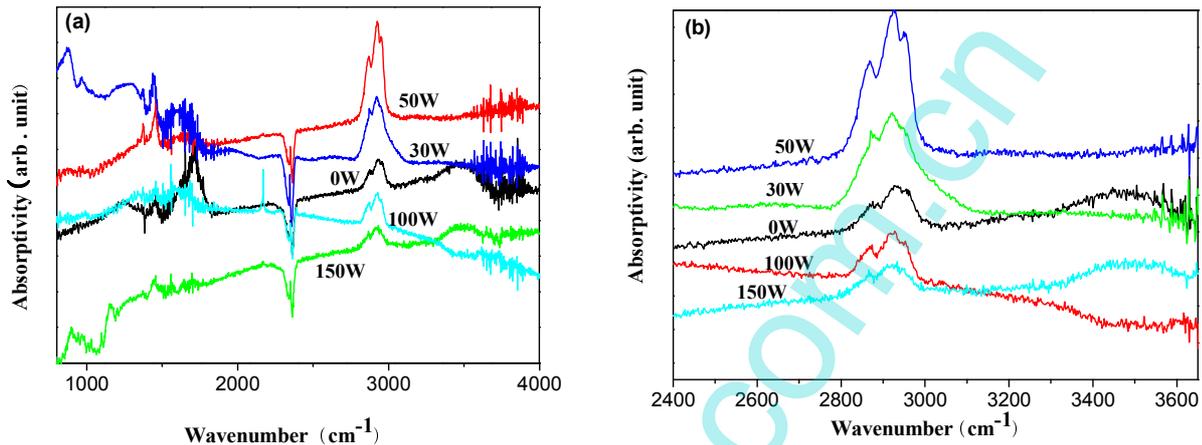
pressure (Pa)	Discharge gas flow rate (sccm)	Microwave power (W)	RF bias power (W)	Deposition temperature (°C)	Exposure time (min)
Base pressure : $5.0 \times 10^{-4}$ Discharge pressure : $2.0 \times 10^{-1}$	CH <sub>4</sub> : 30 Argon : 15	650	0, 30, 50, 100, 150	200	30

The surface morphology of DLC films, which dominates tribological applications, was examined by an atomic force microscope (CSPM5000, BenYuan NanoMeter) operated in the tap mode. The RMS roughness was acquired over a fixed sampling area of  $5 \times 5 \mu\text{m}^2$ . Infrared spectroscopy can easily distinguish C-H  $sp^2$  and  $sp^3$  bonds, thus Fourier transformation infrared spectroscopy (FTIR, Daojin, Japan) was used to detect the C-H bonds stretching vibration affected by bias voltage. The friction coefficient of the films was measured by a ball-on-disk micro-tribometer.

## Results and Discussion

### 1. Chemical structure

FTIR is one of an effective ways to research the structure of DLC films, especial the C-H groups. In the infrared spectrum, the absorption peaks between  $2800\sim 3000\text{cm}^{-1}$  relate to the  $-\text{CH}_n$  stretching vibration modes. Moreover, it can provide the relative contents of  $sp^2\text{-C}$  and  $sp^3\text{-C}$ , as well as the style of C-H bonds formed in DLC films. Generally, the stretching vibrations in the range of  $3000\sim 3100\text{cm}^{-1}$  indicate that the  $sp^2$ : C-H bonds exist in the films; the absorption peaks in the range of  $2800\sim 3000\text{cm}^{-1}$  noted as the carbon atoms mainly bonded with  $sp^3$  orbital configuration<sup>[10]</sup>. The stronger the peak intensity, the higher the hydrogen content, and the more the content of the  $sp^3\text{-C}$  becomes<sup>[11]</sup>.



**Fig. 2** IR absorption spectra of the films deposited at different RF negative bias powers (a-the full spectra; b-the magnified spectra in  $2400\text{--}4000\text{cm}^{-1}$ )

Fig. 2 (a) shows the FTIR spectrum of the DLC films prepared under the different RF negative bias. It can be seen that the stronger absorption peaks were all appeared in the range of  $2800\sim 3000\text{cm}^{-1}$ , and that the C-H stretching vibration absorption peaks locate at lower than  $3000\text{cm}^{-1}$ . This indicates the hydrogen content is very high in the coatings, and the carbon atoms bonded with hydrogen are saturated.

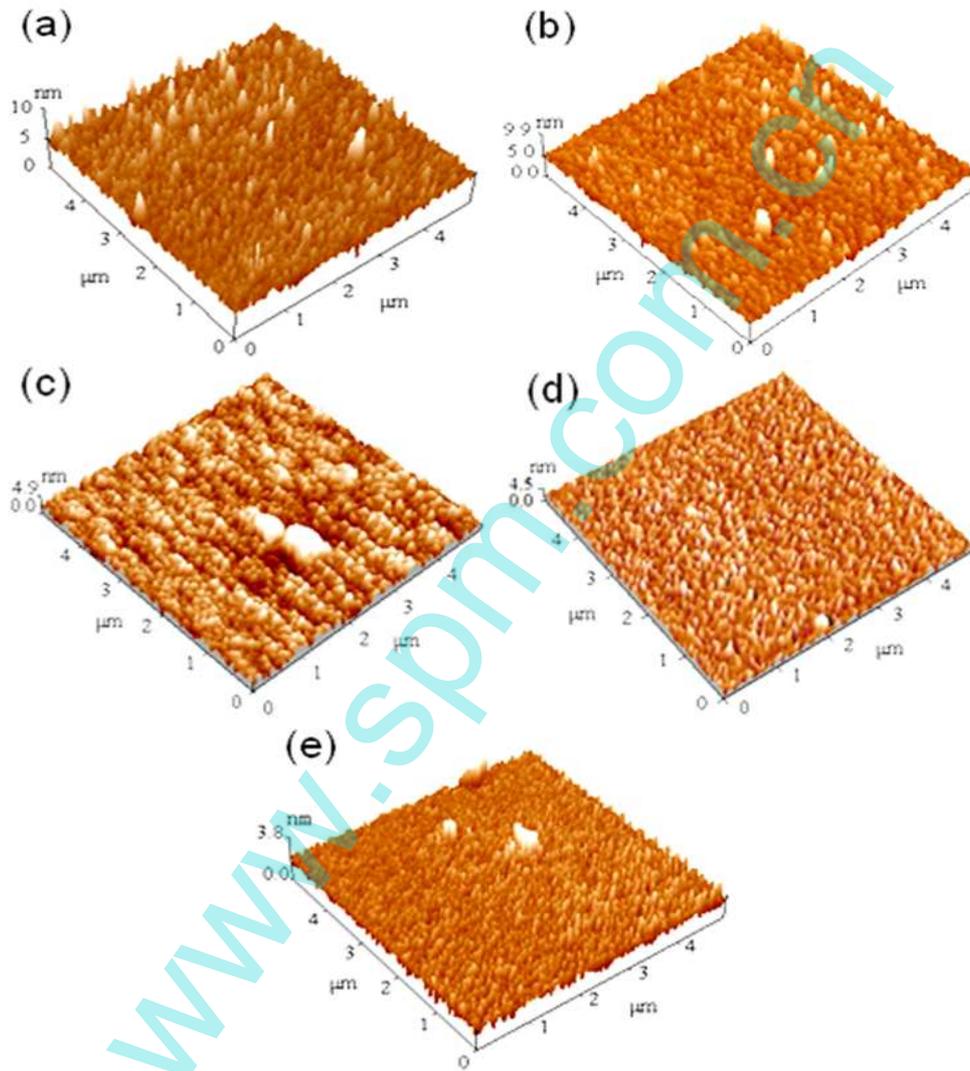
The spectrum between  $2800\sim 3000\text{cm}^{-1}$  are magnified, as shown in Figure 2(b). With the increase of RF bias on the substrate the peak intensity and area of -C-H stretching vibration in spectrum between  $2800\text{cm}^{-1}\sim 3000\text{cm}^{-1}$  increased at the beginning and then decreased. This indicates that the deposition rate of the DLC films depended on RF negative bias. The possible reason of deposition rate decreased with higher RF negative bias is due to the etching strongly. The hydrogen content in the DLC films increased at the beginning and then decreased with increasing the RF negative bias is guessed that increasing the RF negative bias properly can reduced the dangling bond in the structure. As the RF bias becomes high, the flux and the energy of positive ions towards the substrate will increase, the C-H bonds are broken frequently due to the energetic radical bombardment. It also causes the decrease of hydrogen content in films.

### 2. Morphology

Fig. 3 (a)-(e) show the AFM morphologies of the as-deposited DLC films at the different RF negative biases, the scanning scope is  $5\times 5\mu\text{m}^2$ . Obviously, the DLC film is composed of the round nanograins distributing uniformly on substrate. Without the RF negative bias, some micro-particles about several tens of nanometers in size can be observed, and the film is grown in the island model. With the applied RF negative bias, however, the films become smooth and compact, and it became much smooth and compact in the high RF negative bias power condition.

The above phenomenon can be explained by the different deposition mechanisms in the RF bias powers: the growth of the DLC film is caused by a mixture of chemical and physical processes involving both ions and radicals generated in the plasma. The process of DLC film deposition in a

glow discharge is actually a balance of etching and deposition, which mainly depends on the plasma density and ion energy. In addition to the effects of physical sputtering by energetic ions, chemical etching occurring at the surface of the film during growth can also affect the film quality. In our condition, a higher RF negative bias power leads to an increase of the ion density in the plasma. The increase of ionization is accompanied by a higher degree of dissociation in the plasma, i.e. an increase of atomic hydrogen and methyl radical [12]. Atomic hydrogen can both create and passivate dangling bonds. Therefore, with the RF bias the species produce a large flux of atomic hydrogen on the film surface, the etching become significant. The increase of RF negative bias power causes both of plasma density and ion energy increasing, the formed coatings were smooth and compact.



**Fig. 3** AFM images of the films at different RF negative bias powers (a-0W; b-30W; c-50W; d-100W; e-150W)

### 3. Tribological characterization

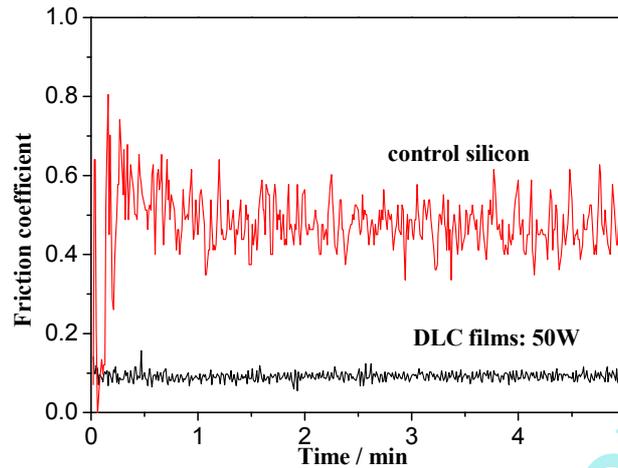


Fig. 4 The friction coefficient of Si and DLC coated on Si

Fig. 4 shows a comparison of the friction coefficient between the as-deposited DLC films under the RF negative biased power of 50W and the silicon. It can be seen that the average friction coefficient of the silicon and the DLC coated Si are 0.48 and 0.12, respectively. This indicates the DLC film has an excellent lubrication performance and can be used as a candidate for a wear resistant material.

Fig. 5 shows the dependent of the friction coefficient on RF negative bias power. The friction coefficient of all deposited DLC substrates is lower than 0.2, but the influence of RF bias on the friction coefficient were remarkable. The coefficient of the DLC films tends to decrease with increasing the RF negative bias power, and reaches a minimum value at 50W condition. After that the friction coefficient increases along with RF negative bias power. This suggests that the RF negative bias greatly increases the reached ion energy at the substrate, and form the more dangling bonds in the surface when the power was lower than 50W, which is beneficial to the hydrogen incorporation saturating the chains and lowering friction coefficient. For the samples prepared under the 100W and 150W conditions, the more cross-linking structure causes the coatings fragile, it was identified by the crack and delaminate observed during the tribological tests. This is attributed to the high energetic ion bombardments of the surface and causing the intrinsic stress in high RF negative bias.

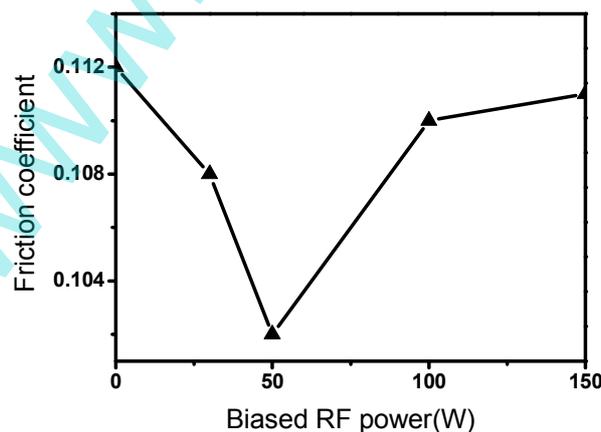


Fig. 5 The friction coefficient of the films versus the RF negative bias powers

### Conclusion

The DLC films were deposited on the single crystalline silicon under the different RF negative bias by ECR plasma source. The FTIR results reveal that the DLC films are hydrogenated carbon. Meanwhile, it is noticed that, without the bias, the surface of the as-deposited film is island growth model and shows the features of the polymer-like. In contrast, the films prepared with the RF bias become smooth and compact. With increasing the RF negative bias, the peak intensities of C-H

stretching vibration in spectrum between  $2800\text{cm}^{-1}\sim 3000\text{cm}^{-1}$  increase at the beginning and then decrease, which causes the variation of friction coefficient in reverse. In 50W RF biased power it is noted that the maximum peak intensity of C-H vibration and the minimum friction coefficient are obtained, which means hydrogenated carbon dominates the coating tribology.

### Acknowledgements

This work is supported by National Natural Science Foundation of China (No. 11175024), Scientific Research Common Program of Beijing Municipal Education Commission (KM201310015006).

### References

- [1] LI Xin, TANG Zhen-An, MA Guo-Ja, Preparation of diamond-like carbon films in methane by electron cyclotron resonance microwave plasma source ion implantation, Chinese Physics Letters. 20 (2003) 692-695.
- [2] A. Dorner, B. Wielage, C. Schürer, Improvement of the corrosion resistance of C/Al-composites by diamond-like carbon coatings, Thin Solid Films. 355 (1999) 214-218.
- [3] Z. Sun, X. Shi, E. Liu, High rate deposition of diamond-like carbon films by magnetically enhanced plasma CVD, Thin Solid Films. 355 (1999) 146-150.
- [4] J. Robertson, Diamond-like carbon, Pure Appl. Chem. 66 (1994) 1789-1796.
- [5] A. Grill, Diamond-like carbon: state of the art, Diamond and Related Materials. 8 (1999) 428-434.
- [6] F. Lang, X. J. Yan, Property, application and preparation of Diamond-like film. Acta Physica Sinica. 48 (1999) 1095-1102.
- [7] H. X Li, T Xu, J. M. Chen, Preparation and characterization of hydrogenated diamond-like carbon films in a dual DC-RF plasma system, J. Phys. D: Appl. Phys. 36 (2003) 3183-3190.
- [8] W. B Yang, S. H. Fan, C. Z. Liu, Investigation of diamond-like-carbon films deposited on glass substrate by using a pulsed high energy density plasma gun, Acta Physica Sinica. 52 (2003) 140-144.
- [9] B. Racine., M. Benlahsen., K. Zellama, Electronic properties of hydrogenated amorphous carbon films deposited using ECR-RF plasma method, Diamond and Related Materials. 10 (2001) 200-206.
- [10] A. Grill, V. Patel, Characterization of diamond-like carbon by infrared spectroscopy, Applied Physics Letters. 60 (1992) 2089-2092.
- [11] B. Dischler, A. Bubenzer, P. Koidl, Hard carbon coatings with low optical absorption, Applied Physics Letters. 42 (1983) 636-638.
- [12] W. Zhang, Y. Catherine, Deposition of carbon films by the dissociation of methane in r.f. discharge, Surface and Coatings Technol. 47 (1991) 69-83.

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10.4028/www.scientific.net/AMM.423-426.756

**DOI References**

- [1] LI Xin, TANG Zhen-An, MA Guo-Ja, Preparation of diamond-like carbon films in methane by electron cyclotron resonance microwave plasma source ion implantation, *Chinese Physics Letters*. 20 (2003) 692-695.  
<http://dx.doi.org/10.1088/0256-307X/20/5/329>
- [2] A. Dorner, B. Wielage, C. Schürer, Improvement of the corrosion resistance of C/Al-composites by diamond-like carbon coatings, *Thin Solid Films*. 355 (1999) 214-218.  
[http://dx.doi.org/10.1016/S0040-6090\(99\)00497-6](http://dx.doi.org/10.1016/S0040-6090(99)00497-6)
- [3] Z. Sun, X. Shi, E. Liu, High rate deposition of diamond-like carbon films by magnetically enhanced plasma CVD, *Thin Solid Films*. 355 (1999) 146-150.  
[http://dx.doi.org/10.1016/S0040-6090\(99\)00484-8](http://dx.doi.org/10.1016/S0040-6090(99)00484-8)
- [4] J. Robertson, Diamond-like carbon, *Pure Appl. Chem*. 66 (1994) 1789-1796.  
<http://dx.doi.org/10.1351/pac199466091789>
- [5] A. Grill, Diamond-like carbon: state of the art, *Diamond and Related Materials*. 8 (1999) 428-434.  
[http://dx.doi.org/10.1016/S0925-9635\(98\)00262-3](http://dx.doi.org/10.1016/S0925-9635(98)00262-3)
- [9] B. Racine., M. Benlahsen., K. Zellama, Electronic properties of hydrogenated amorphous carbon films deposited using ECR-RF plasma method, *Diamond and Related Materials*. 10 (2001) 200-206.  
[http://dx.doi.org/10.1016/S0925-9635\(00\)00468-4](http://dx.doi.org/10.1016/S0925-9635(00)00468-4)
- [10] A. Grill, V. Patel, Characterization of diamond-like carbon by infrared spectroscopy, *Applied Physics Letters*. 60 (1992) 2089-(2092).  
<http://dx.doi.org/10.1063/1.107098>
- [11] B. Dischler, A. Bubenzer, P. Koidl, Hard carbon coatings with low optical absorption, *Applied Physics Letters*. 42 (1983) 636-638.  
<http://dx.doi.org/10.1063/1.94056>
- [12] W. Zhang, Y. Catherine, Deposition of carbon films by the dissociation of methane in r. f. discharge, *Surface and Coatings Technol.* 47 (1991) 69-83.  
[http://dx.doi.org/10.1016/0257-8972\(91\)90269-3](http://dx.doi.org/10.1016/0257-8972(91)90269-3)